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Laboratory assessment of atrazine and fluometuron degradation in soils from a constructed wetland

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Abstract

Constructed wetlands offer promise for removal of nonpoint source contaminants such as herbicides from agricultural runoff. Laboratory studies assessed the potential of soils to degrade and sorb atrazine and fluometuron within a recently constructed wetland. The surface 3 cm of soil was sampled from two cells of a Mississippi Delta constructed wetland; one shallow area disturbed only hydrologically, and the second excavated to provide greater water-holding capacity. The excavated area was more acidic on average (pH 4.85 versus 5.21), but otherwise the physical properties and general microbial enzyme activities in the two areas were similar. Soils were treated with 84 and 68 $\mu g\,kg^{-1}$ soil ^{14}C-ring labeled atrazine and fluometuron, respectively, and incubated under either saturated (88% moisture, w:w) or flooded (1 cm standing water) conditions. Soils were sampled over 32 days and extracted for herbicide and metabolite analysis. Under saturated conditions, fluometuron metabolized to desmethylfluometuron (DMF) with a half-life equal 25–27 days. However, under flooded conditions, the half-life of fluometuron was more than 175 days. Atrazine dissipated rapidly in saturated and flooded soil with a half-life of approximately 23 days, but only 10% of atrazine was mineralized to CO_2. The overall atrazine and fluometuron dissipation rates were similar between the two cells, but each area had a different pattern of metabolite accumulation. The major route of atrazine dissipation was incorporation of atrazine residues into methanol-nonextractable (soil-bound) components, with minimal extractable metabolite accumulation. A mixed-mode extractant (potassium phosphate:acetonitrile) recovered greater amounts of ^{14}C-residues from atrazine-treated soils, suggesting that hydrolysis of atrazine to hydroxylated metabolites was a major component of the bound residues. These studies indicate the potential for herbicide dissipation in wetland soils and a differential effect of flooding on the fate of these herbicides.
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Keywords: Atrazine; Fluometuron; Wetland soils; Herbicide fate; Herbicide sorption; Herbicide degradation

1. Introduction

Constructed wetlands offer the potential for the removal of contaminants from point sources, such as municipal and industrial wastes (Green et al., 1996; Scholz, 2003; Steinmann et al., 2003; Ye et al., 2003). They are commonly employed to lower biological oxygen demand and remove suspended solids and nitrates from wastewater (Schaafsma et al., 2000; Kao et al., 2001; Cameron et al., 2003). The efficiency and mechanisms of xenobiotic processing by constructed wetlands is less well understood.

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Nonpoint source contamination of surface waters by agrochemicals in runoff is a major cause of impaired water quality in the USA. The development of management practices to mitigate this contamination is a high priority. Edge of field practices such as vegetative filter strips (Merise et al., 1999; Staddon et al., 2001), maintenance of riparian zones and wetlands (Reungsang et al., 2001), and the use of vegetated ditches (Moore et al., 2001) are being considered for removal of agrochemicals in surface runoff before introduction into lakes, streams and rivers. Constructed wetlands may be a viable management tool for mitigating herbicide contamination from nonpoint source runoff. The fate of the widely used herbicide atrazine [6-chloro-*N*-ethyl-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] has been experimentally assessed in wetlands both in situ (Lee et al., 1995; Runes et al., 2003) and in microcosms using soils collected from wetland sites (Entry and Emmingham, 1996; Anderson et al., 2002). Factors including history of herbicide exposure (Anderson et al., 2002), and type of vegetation (Lee et al., 1995; Entry and Emmingham, 1996) can effect atrazine degradation in wetland systems. Fluometuron [*N*,*N*-dimethyl-*N*′-(3-trifluoroemethylphenyl)urea], is predominantly used in cotton production in the Southeastern USA and has been observed in surface waters in the Misssissippi Delta (Locke et al., 2002). Laboratory studies have indicated that fluometuron is rapidly degraded in a soil from a forested riparian zone (Shankle et al., 2001; Locke et al., 2002).

The Mississippi Delta Management Systems Evaluation Areas (MD-MSEA) project was established to quantitatively assess the value of best management practices (BMPs) in improving the quality of agricultural runoff water. Studies from the MD-MSEA have documented the benefits of other BMPs (Rebich and Knight, 2001; Staddon et al., 2001). A wetland was recently constructed at one MD-MSEA study site at Beasley Lake watershed, Sunflower County, Mississippi, USA to evaluate its potential as a BMP. After 1 year of establishment of this constructed wetland, we have reported changes in the vegetation and hydrology as well as shifts in the microbial community structure (Weaver et al., 2003). The objective of this study was to assess the impact of flooding on the environmental fate of atrazine and fluometuron in soil from a recently constructed wetland.

2. Materials and methods

2.1. Study site and soils

A constructed wetland was established in April of 2003 at an inlet to Beasley Lake, an oxbow lake near the Sunflower River in Sunflower county Mississippi. The constructed wetland consists of a small sediment trap; a long, shallow cell; and a deeper, excavated cell (Fig. 1).

Soil and water samples were collected from four replicate points of the excavated and shallow (unexcavated) cell. About 1 kg of moist soil was collected from the upper 3 cm layer using a trowel and stored at 4 °C until the experiment was initiated. Initial soil moisture content was high and variable, thus soils were centrifuged to remove excess free water, leaving soils ranging from 56% to 82% moisture content.

2.2. Soil properties

The texture and chemical properties of the soil, a Dowling clay (very-fine smectitic, thermic Typic Endoaqualfs; hydric, clayey alluvium of recent Holocene age) (Soil Survey Staff, 1959) were characterized prior to wetland construction and are reported in Weaver et al. (2003). Fluorescein diacetate (FDA) enzyme assays (modified from Schnürer and Rosswall, 1982) were conducted as a general indicator of soil microbial hydrolytic activity for esterase, lipase and protease. Dehydrogenase

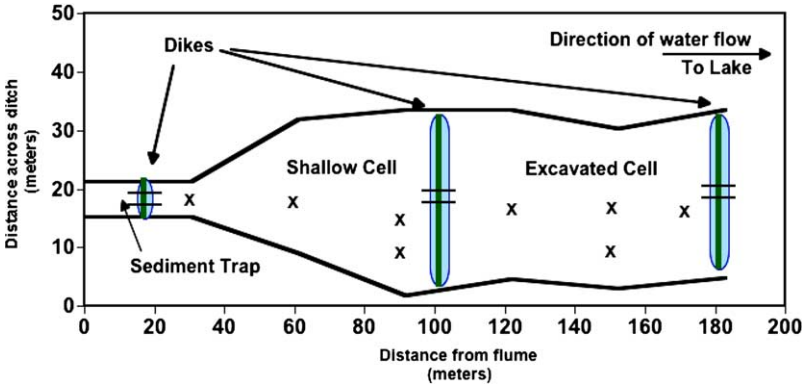

Fig. 1. Sampling sites at the Beasley Lake constructed wetland. Sampling points are marked with ×.

was measured using triphenyl tetrazolium chloride (TTC) as substrate and yeast extract as a carbon source (modified from Casida, 1977; Staddon et al., 2001). All enzyme assays were conducted using 4 g of soil (wet weight). Electrical conductivity and pH were recorded from a 2:1 water to soil slurry. Elemental carbon and nitrogen content in the soils were measured on dried, milled subsamples using a Flash EA 112 elemental analyzer (CE Elantech, Lakewood, New Jersey).

2.3. Soil and water incubation

Moist soil equal to 30 g dry weight from the four replicate samples from each wetland cell was treated with either ^{14}C-ring labeled atrazine or fluometuron. Radiolabeled atrazine had a specific activity = 690 mBq mmol^{-1} and greater than 97% radioactive purity based on TLC (thin layer chromatography) analysis, (Sigma Chemical Co. St. Louis, MO). The radiolabeled fluometuron had a specific activity of 652 mBq mmol^{-1} and greater than 98% radioactive purity based upon TLC analysis (Syngenta, Greenwood, NC). Treated soil was then adjusted to 88% moisture (saturated) or flooded by adjusting to 88% moisture and then adding an additional 30 ml of water to flood to a depth of about 1 cm (flooded). Atrazine was added to bring the soil concentration to 84 μg kg^{-1} dry soil equivalent (167 Bq g^{-1} soil). Fluometuron was added at 68 μg kg^{-1} soil (117 Bq g^{-1} soil). These concentrations applied were less than 5% of agronomic application rates and were designed to mimic concentrations that may result from agricultural runoff.

Recovery of methanol-extractable herbicide and metabolites was used to characterize dissipation in fluometuron-treated soils. Eight 250 ml, polypropylene screw cap centrifuge bottle incubations were initiated for each sample point within the constructed wetland. Flooded and saturated treatments were sampled at 0, 8, 17, and 32 days after the herbicide fortification. Replicate polypropylene flasks without herbicides were initiated under saturated and flooded conditions to monitor redox potential. Mineralization (i.e. degradation to $^{14}CO_2$) was determined for atrazine-treated soil and water, using biometer flasks (Bartha and Pramer, 1965) in addition to recovery of methanol-extractable herbicide from polypropylene screw cap bottles. Biometer flasks were also established with water collected at each wetland sampling point. Thirty milliliters of water were added per flask, followed by aqueous atrazine to achieve a concentration of 42 μg l^{-1} (84 Bq ml g^{-1}). Thus, the atrazine experiment consisted of six centrifuge bottle incubations (three flooded and three saturated soil treatments, sampled at 0, 8, and 17 days after treatment) and one flooded, one saturated and one with only water biometer flasks for each wetland sampling point. Thirty grams of oven dried equivalents of soil were added to each bottle or flask. The herbicide was added in 2.0 ml aqueous solution and deionized water (0–7.7 ml) was added to each soil to achieve a moisture content of 88%. For the flooded treatment, an additional 30 ml water (collected from the sample site) were added to achieve about 1 cm of water above the soil level. Atrazine mineralization in the water samples was also determined in biometer flasks incubated at 26 °C. The side arm traps of the flask were filled with 10 ml sodium hydroxide (1 N), which was replaced with fresh solution every 2–5 days. $^{14}CO_2$ trapped in the sodium hydroxide was determined on duplicate 1 ml aliquots by liquid scintillation spectroscopy (LCS) (Packard Tri-Carb liquid scintillation analyzer, Packard Biosciences, Meriden CT) using 15 ml Hionic scintillation fluid (Packard Biosciences) per sample.

2.4. Extractions and analysis

To recover herbicides and metabolites, treated soils were agitated with 100 ml of 100% methanol for 20 h, centrifuged for 10 min at 6000 × *g*, and the supernatant was removed. A second methanol extraction was repeated for all samples. Experiments in our laboratory and by others (Seybold et al., 2001) indicated that the highest efficiency of both atrazine and fluometuron recovery is with about 80:20 methanol:water (v:v). As initial soil moisture was high, no additional water was added. No reference standards were included in extractions, however, during the first 17 days of the study a mass balance of recovery of radioisotope was never less than 92%. All 0-day samples were extracted within 4 h of treatment. Methanol extracts were combined, weighed and a 1 ml aliquot taken for radioactivity quantification by LSC using Ecolume scintillation fluid (ICN Costa Mesa, California). The remaining extracts were concentrated by rotary evaporation, diluted in 150 ml of water, acidified with 100 μl 1.0 N HCl, and further concentrated on a 3-ml C18 solid phase extraction (SPE) column (Bakerbond, JT Baker Phillipsburg, PA) preconditioned by eluting with 9 ml methanol followed by 25 ml of distilled water under negative pressure (−20 kPa). The herbicide and metabolites were eluted from the SPE column with 4 ml of methanol and concentrated to 1.5 ml under N_2 gas. More than 95% of radioactivity was bound and eluted from the SPE column using this method for both herbicides. Herbicides and metabolites recovered in the methanol extracts were determined using TLC and linear imaging scanning (Bioscan 200 Imaging Scanner, Bioscan Washington, DC). Radiolabeled herbicide and metabolite standards were separated by TLC and a peak area for parent and metabolites integrated by the scanner. Every plate included a lane of radiolabeled atrazine or fluometuron, as an internal standard to verify R_f of the parent. Methodology for TLC analysis of atrazine was according to Blumhorst and Weber (1994) and

fluometuron according to Zablotowicz et al. (2000) with TLC plates (Whatman, LKF, Clifton, NJ) conditioned at 80 °C for at least 4 h prior to use. TLC plates were developed in a twin trough TLC tank (CaMag Scientific Inc., Wilmington, NC.) to facilitate vapor equilibration. One hundred microliters aliquots were spotted on 250 μm think silica gel plates. TLC plates for fluometuron analysis were developed 10 cm using chloroform:ethanol (95:5 v:v) solvent. TLC plates for atrazine analysis were developed to 10 cm using toluene:ethyl acetate (50:50 v:v) solvent. R_f values for standards were: fluometuron = 0.58; desmethyl fluometuron (DMF) = 0.30; trifluoromethylphenylurea = 0.58; and trifluoromethylaniline = 0.76 (Zablotowicz et al., 1998, 2000). R_f values for atrazine standards were atrazine = 0.67, deethyl atrazine (DEA) = 0.40, deisopropyl atrazine (DIA) = 0.23, and hydroxyatrazine = 0.00 (Blumhorst and Weber, 1994). Nonextractable radioactivity remaining in soils following two methanol extractions (bound fraction) was determined by oxidation (Packard 306 oxidizer) and LSC. Five grams of air dried, atrazine-treated soils that were previously extracted twice with methanol (100%) were re-extracted with either 10 ml of methanol:water (8:2) or 0.5 M dibasic potassium phosphate (pH 7.5):acetonitrile (3:1) for 24 h in 25 ml Corex tubes. Following extraction the tubes were centrifuged (10 min, 10 000 × g) and radioactivity in the supernatant determined by LSC. Extractable atrazine and fluometuron data were fit to first-order kinetics using the PCSAS NLIN procedure (SAS, Cary NC). The first-order degradation rate constant (K) and the 95% confidence interval were calculated using the NLIN procedure, and the half-life ($T_{1/2}$) was calculated from K.

2.5. Herbicide sorption and desorption

Batch sorption techniques were used to characterize atrazine and fluometuron sorption and desorption in soils from the constructed wetland (Locke et al., 1997). A 1:2 ratio of soil to solution was used with four replicates per sample. Five grams of air dried was weighed into 25 ml Corex centrifuge tubes with Teflon lined caps. Then milliliters of atrazine or fluometuron (1.34 μM, 1.0 μM technical grade, 0.34 μM ^{14}C-labeled herbicide) in 0.01 M $CaCl_2$ was added and the suspensions were equilibrated on a rotary shaker at 25 °C for 24 h. Following equilibration, samples were centrifuged for 10 min at 15 000 × g, and 12 °C. The supernatant was removed, weighed and aliquots counted for radioactivity by LSC. Herbicide sorption was defined as the difference between input concentration and supernatant concentration after the equilibration. Desorption assays were than conducted in two 24 h equilibrations with 0.01 M $CaCl_2$. Atrazine and fluometuron sorption was characterized by the distribution coefficient at one standard concentration. $S = K_dC$ where S is the amount of herbicide sorbed to soil (μmol kg^{-1}), K_d is the distribution coefficient, and C is the concentration of herbicide in solution at equilibria (μmol l^{-1}).

3. Results and discussion

3.1. Soil properties

Observed properties of soil from the shallow and excavated areas are summarized in Table 1. Soil extracted from both areas of the constructed wetland were similar in conductivity, and enzymatic properties. However, the shallow cell was less acidic and had a greater percent carbon and nitrogen composition. The excavated cell was less densely vegetated than the shallow cell, which may have contributed to the difference in the observed carbon. The redox potential for treatments with soil from excavated area was initially below 100 mV despite the mixing and disturbance in establishing the incubation flasks. The redox potential of soils from the excavated cell ranged from 27 to 54 mV compared to 340 to 353 mV for soils in the shallow cell (Table 1). However after the first weeks' incubation, the difference in redox potential between soils from the two cells was much smaller (Fig. 2). After incubation for 2 weeks, the redox potential for all treatments was below 100 mV.

3.2. Fate of atrazine

Atrazine dissipated relatively rapidly with a half-life of 17.7–24.8 days. Atrazine dissipation was more rapid under saturated than flooded conditions (Table 2). About 19–24% of the ^{14}C added was recovered by methanol extractions at the end of the incubation regardless of treatment (Fig. 3). Less than 3% of added herbicide accumulated as DEA, DIA or polar hydroxylated metabolites (data not shown). At day 0, methanol

Table 1
Chemical, biological and physical characterstics of soils from shallow and excavated cells of the Beasley constructed wetland

Characteristic	Shallow	Excavated
pH (water)	5.21 (0.02)[a]	4.85 (0.20)
Electrical conductivity (mS/cm)	199 (27)	218 (9)
Initial moisture (%)	74 (5)	63 (3)
TTC dehydrogenase activity	276 (107)	273 (73)
FDA hydrolytic activity	3679 (997)	4102 (376)
Carbon (%)	2.91 (0.15)	2.01 (0.16)
Nitrogen (%)	0.51 (0.02)	0.35 (0.05)
Initial ORP	340 mV	54 mV

TTC nmol triphenyl tetrachloride g^{-1} h^{-1}, FDA nmol fluorescein diacetate g^{-1} h^{-1}.

[a] Mean values. Standard error given in parentheses.

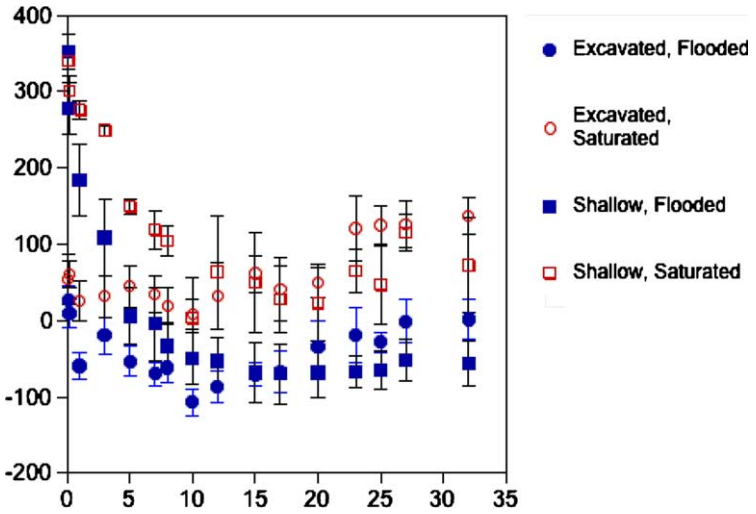

Fig. 2. Redox potential in soil incubation. Bars represent standard error.

Table 2
Kinetic parameters of atrazine and fluometuron degradation in soils from two constructed wetland cells as affected by flooding status

Wetland cell/treatment	Atrazine			Fluometuron		
	C_o	K	Half-life (days)	C_o	K	Half-life (day)
Shallow/flooded	70.5 (1.7)[a]	0.0497 (0.0026)	22.4	91.5 (2.7)	0.0058 (0.0017)	172[b]
Shallow/saturated	68.3 (3.1)	0.0542 (0.0058)	18.5	96.6 (3.7)	0.0358 (0.0035)	27.3
Excavated/flooded	73.9 (2.3)	0.0402 (0.0036)	24.8	92.3 (1.8)	0.0653 (0.0011)	223[b]
Excavated/saturated	74.2 (2.2)	0.0564 (0.0039)	17.7	95.2 (3.4)	0.0389 (0.0034)	25.2

[a] Mean values. Standard error given in parentheses.
[b] Extrapolated half-life from measured K values. Half-life exceeded experimental duration.

extraction recovered only 73–79% of the initial ^{14}C applied to atrazine-treated soils, and 17–20% of applied ^{14}C was accounted for in the methanol-unextractable residues. The major fate of atrazine regardless of flooding or cell was incorporation into methanol-unextractable soil components, (55–67%), with a small fraction (9–12%) being completely mineralized (Fig. 4). The methanol-extracted soil was re-extracted with either a mixed-mode solvent (acetonitrile/phosphate buffer) or 80% methanol to elucidate the nature of bound atrazine residues (Lerch et al., 1997). After 32 days, 18–25% of the applied ^{14}C was recovered in the mixed-mode solvent compared to 3–5% in aqueous methanol (Table 3). Thus, a major component of the methanol-unextractable atrazine residues in soil are most likely the polar, hydroxylated atrazine metabolites (Lerch et al., 1997, 1999).

In incubations with water collected from the wetlands, 80% and 87% of the atrazine added was recovered from water from the shallow and excavated cell respectively at day 32 (data not shown). About 9% and 3% of the radioactivity was recovered as metabolites from water from the shallow and excavated cell respectively at day 32 (data not shown), and 6–7% mineralized during the study (Fig. 4). Thus, only limited atrazine degradation occurred in water collected from the wetlands compared to soil.

The rates of mineralization observed in these studies are much lower than reported in soil from a constructed wetland from Ohio (Anderson et al., 2002). Sediment from that wetland mineralized up to 70–80% of the applied atrazine in a 30 days incubation. Anderson et al. (2002) suggested that the high mineralization rate might be attributable to the historic annual inputs of atrazine and the maintenance of populations of atrazine-degrading bacteria. In contrast, the watershed that supplies the wetland in the present study had only one atrazine exposure in the past 10 years. Additionally, the relatively low rate of mineralization in the present study may be related to this soil's high affinity for atrazine, leaving a smaller component bioavailable for mineralization. Furthermore, these soils were fairly acidic, which may have facilitated acid hydrolysis of atrazine to hydroxy-derivatives (Blumhorst and Weber, 1994; Comber, 1999) and consequent binding of hydrolyzed intermediates. Studies by Houot et al. (2000) indicated that soils with a pH below 6.5 had limited mineralization potential, with the

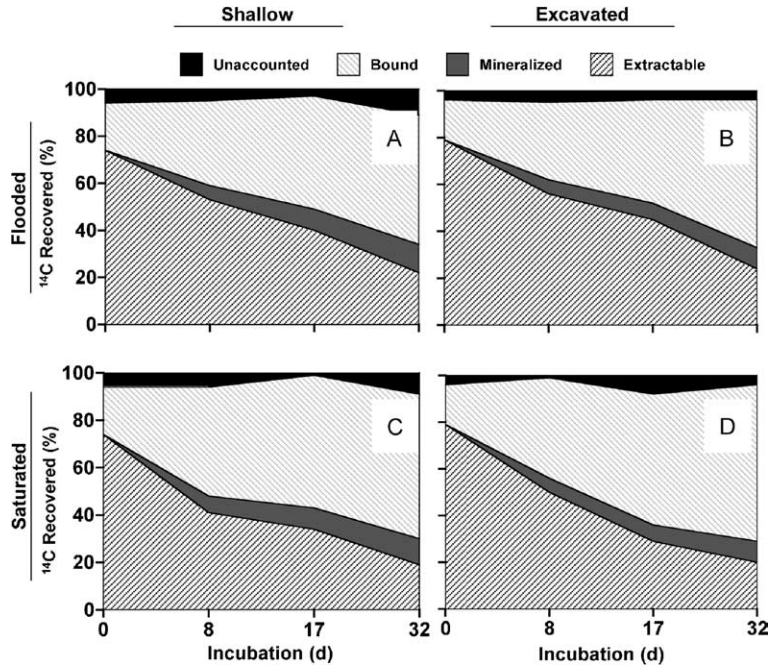

Fig. 3. Recovery of atrazine. Soil from the shallow wetland cell in (A) and (C). Soil from the excavated wetland cell in (B) and (D). Incubated under flooded conditions in (A) and (B). Incubated under saturated conditions in (C) and (D).

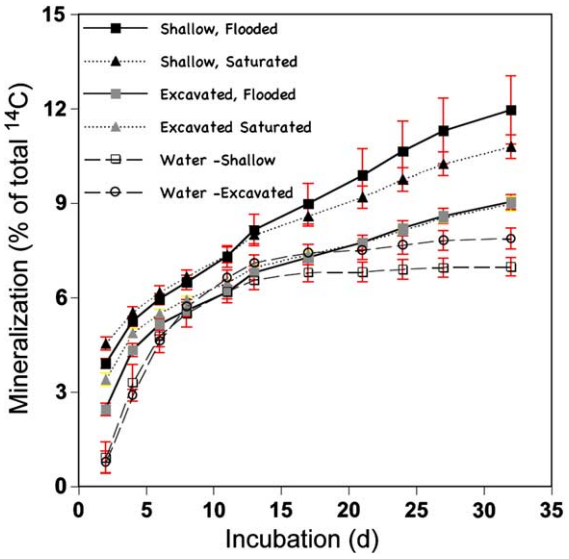

Fig. 4. Mineralization of atrazine.

major fate of atrazine being transformed into bound nonextractable residues.

3.3. Fate of fluometuron

Fluometuron recovery via methanol extraction at day 0 was 91–92% while atrazine recovery was only 73–79%. Fluometuron dissipated rapidly in soils incubated under saturated conditions, with less than 30% recovered by methanol extraction after 32 days, while under flooded conditions fluometuron was more persistent with >80% recovered after 32 days (Fig. 5). The $T_{1/2}$ for fluometuron under saturated conditions is similar to that reported for soils collected from a riparian zone in this watershed site, however inhibition of fluometuron degradation was not observed at higher moisture contents (Shaw et al., 2001). The kinetics of fluometuron dissipation were described using a first-order model, and were similar in soils from both cells incubated under a given flooding regime (Table 2). Approximately 33% of the applied fluometuron was recovered as DMF after 32 days incubation in saturated soils compared to 8% in flooded soils. No other fluometuron metabolites were detected. There was only a limited increase (4–5%) in methanol-unextractable ^{14}C fluometuron residues following a 32 days incubation under flooded conditions, while 22–36% of the initial ^{14}C applied occurred in the bound fraction under saturated conditions. Also, under saturated conditions a greater ^{14}C content was found in the bound fraction in the shallow cell, while greater DMF was recovered in the excavated cell. Greater DMF was produced in the saturated treatments than in the flooded treatments, suggesting that *N*-dealkylation, or the organism(s) involved are inhibited by the low redox potential of flooded conditions. *N*-Dealkylation is typically considered an aerobic process catalyzed

Table 3
Atrazine residues in wetland soils as affected by incubation time and flooding

Wetland area/incubation time	Percent of initial ^{14}C-atrazine added		
	Bound[a]	Mixed mode extractable[b]	Methanol extractable[c]
Shallow area–flooded			
Day 0	20.4 (0.9)	14.3	6.2
Day 8	36.3 (1.7)	9.8	4.1
Day 17	47.5 (3.4)	12.9	3.0
Day 32	55.4 (10.3)	18.0	3.1
Shallow area–saturated			
Day 0	20.4 (0.9)	14.3	6.2
Day 8	46.3 (4.1)	14.3	6.4
Day 17	56.1 (2.3)	17.2	5.9
Day 32	61.1 (4.5)	19.0	5.0
Excavated area–flooded			
Day 0	17.2 (3.3)	14.1	4.0
Day 8	33.0 (3.9)	13.1	4.7
Day 17	44.1 (5.9)	13.9	3.0
Day 32	63.3 (7.1)	19.6	3.1
Excavated area–saturated			
Day 0	17.2 (3.3)	14.1	4.0
Day 8	43.5 (4.2)	17.0	5.2
Day 17	55.6 (4.5)	20.8	4.3
Day 32	67.3 (4.0)	24.7	5.2

[a] Bound residues defined as percent of added ^{14}C released by oxidation after two methanol extractions. Mean values are presented with standard deviations in parentheses.

[b] ^{14}C extracted by mixed-mode extractant [0.5 M dibasic potassium phosphate (pH 7.5):acetonitrile (3:1)] after two methanol extractions.

[c] ^{14}C extracted by 80% methanol after two methanol extractions.

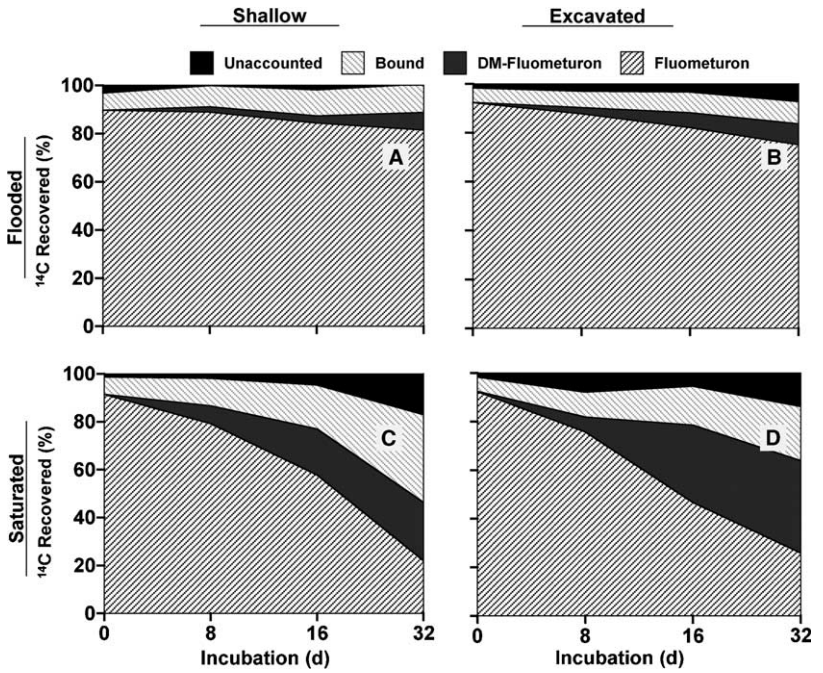

Fig. 5. Recovery of fluometuron. Soil from the shallow wetland cell in (A) and (C). Soil from the excavated wetland cell in (B) and (D). Incubated under flooded conditions in (A) and (B). Incubated under saturated conditions in (C) and (D).

by cytochrome P450 monooxygenases, where the *N*-dealkylated metabolites of fluometuron are eventually metabolized to trifluoromethylaniline, which is readily incorporated into bound residues via oxidative coupling reactions with soil organic matter (Zablotowicz et al., 1998, 2000). About 50% greater radioactivity was incorporated into bound residues in soils from the shallow cell under saturated conditions compared to the excavated cell. This difference may be attributable to the greater organic carbon content of the shallow versus excavated cell.

3.4. Sorption of atrazine and fluometuron

Following a 24 h equilibration with 1.35 μM atrazine or fluometuron there was a greater amount of atrazine sorbed compared to fluometuron (Table 4), based upon K_d values or the % of herbicide sorbed. Similar K_d values for atrazine sorption were found in soils from the excavated and shallow areas, while more fluometuron was sorbed in the soil from the shallow area than the excavated soils. The greater sorption of fluometuron in the shallow cell than the excavated cell corresponds with the higher organic carbon content of the shallow cell. When the K_d values are normalized for organic carbon (K_{oc}), similar values are observed for fluometuron in excavated and shallow cell soils. However, atrazine K_{oc} values are higher in the excavated cell compared to the shallow cell, suggesting other factors, such as pH contribute to the atrazine sorption potential of the excavated cell soils. Atrazine sorption has been shown to increase with lower soil pH (Clay et al., 1988). Following two 24 h desorption steps in $CaCl_2$, only 39–44% of the atrazine adsorbed was released into solution, while 75–86% of adsorbed fluometuron was released, indicating that adsorbed fluometuron would be more readily bioavailable for degradation compared to atrazine. The relative sorption and desorption potential of atrazine and fluometuron using batch methods, agree with the ^{14}C-degradation studies where the major fate of atrazine was the formation of bound residues, while bound residues were the major fate of fluometuron only following initial metabolism.

Table 4
Atrazine and fluometuron sorption and desorption in soils from an excavated and shallow cell of a constructed wetland

	Atrazine		Fluometuron	
	Excavated	Shallow	Excavated	Shallow
K_d[a]	6.2 (0.4)[b]	6.8 (1.0)	2.1 (0.2)	2.8 (0.1)
K_{oc}	313 (46)	235 (35)	106 (7)	96 (7)
	Percent recovery of herbicide following equilibration[c]			
Sorbed	76 (3)	77 (3)	51 (7)	58 (1)
Desorbed	30 (5)	34 (4)	44 (1)	44 (1)

[a] K_d and K_{oc} expressed as $\mu M\,kg^{-1}$.
[b] Standard deviations of four replicates are provided within parentheses.
[c] Based on recovery and measurement of radioactivity.

4. Conclusions

These studies indicate the differential capability of wetland soils for herbicide processing and illustrate the strong influence hydrology plays on the environmental fate of atrazine and fluometuron. Soil from this constructed wetland processed and/or sequestered atrazine under both flooded and saturated soil conditions. In contrast, fluometuron was degraded rapidly under saturated conditions, but was very persistent under flooded conditions.

The removal of atrazine was faster in saturated soils than in flooded soils, consistent with a redox-related chemical or biotic process. Only a small (9–12%) amount of atrazine was mineralized. The predominant fate of atrazine in this system was incorporation into methanol-nonextractable soil residues. Extraction of the soil with other solvent systems suggested that the soil bound fraction was largely in the form of polar, hydroxylated products. Although hydroxyatrazine can be formed from bacterial-mediated enzymatic dechlorination by amidohydrolases (Mandelbaum et al., 1995; Topp et al., 2000; Rousseux et al., 2001), chemically-mediated hydrolytic atrazine dechlorination is also well established (Blumhorst and Weber, 1994; Comber, 1999), especially in acidic soils such as present in this wetland.

The rate of fluometuron dissipation observed in these wetland soils under saturated conditions are similar to those observed for surface soils under agronomic conditions (Zablotowicz et al., 2000; Locke et al., 2002). The formation and accumulation of DMF under saturated conditions indicate a potential for rapid metabolic degradation in soils under saturated conditions, but DMF did not accumulate under flooded conditions. Although the redox of saturated wetland soil attained reducing conditions, there may have been sufficient aerobic microsites present to facilitate an aerobic process such as *N*-dealkylation. Fluometuron degradation in wetland soil in situ may not be as inhibited under flooded conditions, because wetland vegetation may facilitate oxygenation of soil (Colmer, 2003).

In saturated soil from the shallow area a greater portion of fluometuron was incorporated into bound residues but in soil from the excavated area more fluometuron was converted to DMF. This difference may be attributed to differences in carbon content of soils from the different cells.

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